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The Resources Agency
DEPARTMENT OF FISH AND GAME

**PRELIMINARY HAZARD ASSESSMENT
OF THE HERBICIDE GLYPHOSATE
TO AQUATIC ORGANISMS**



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Preliminary Hazard Assessment of the Herbicide Glyphosate
to Aquatic Organisms

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INTRODUCTION

This report has been prepared to assess potential toxicological hazards posed by glyphosate to aquatic life in treatment rates required to control the exotic plant *Arundo donax*. *Arundo donax*, also known as giant reed or wild cane, has invaded riparian habitat throughout California. The nonchemical effects of vegetation management on fish and wildlife habitat are beyond the scope of this document.

Glyphosate is a non-selective herbicide used to control broadleaf weeds and grasses in many food crops, ornamentals, lawns and turf, residential areas, greenhouses, forest plantings, and industrial rights-of-way. In 1994, the most recent year for which reliable data are available, 3,729,000 lbs of glyphosate were used in California (DPR n.d.).

Glyphosate is the active ingredient of the herbicides Rodeo^R and Roundup^R. Rodeo^R and Roundup^R are 53.8 and 41% active ingredient, respectively. In addition to glyphosate, Roundup^R contains the surfactant MON0818.

Application methods for Roundup[®] and Rodeo[®] include broadcast and spot foliar sprays by ground equipment, cut stump treatments, wiper treatments, and aerial application. Rodeo[®] is registered for use in aquatic sites, and is the herbicide most commonly used to treat *Arundo donax*. For foliar treatments of *Arundo donax*, a 1.5% solution of Rodeo[®] plus a 0.5% v/v of a non-ionic surfactant is applied. For broadcast treatment with Rodeo[®], 7.5 pints/acre plus a 0.5% v/v non-ionic surfactant is applied. For cut stump treatments, Rodeo[®] is applied at full strength onto the freshly cut surface. Treatment rates for Roundup[®] are 2% v/v solution for spot treatment, 5 quarts/acre for broadcast treatment, and full strength treatment for cut stump treatment. Applications of either herbicide usually take place in late summer or early fall.

The U.S. Environmental Protection Agency (U.S. EPA) has not recommended water quality guidelines for glyphosate for the protection of aquatic organisms.

Hazards from glyphosate to aquatic life were assessed by comparing acute and chronic studies and environmental fate data with the application rates proposed for the treatment of *Arundo donax*.

ENVIRONMENTAL FATE

Glyphosate is resistant to chemical degradation and photodegradation in soil, but is completely and rapidly degraded by microorganisms (U.S. Department of Agriculture (USDA) 1984). Aerobic soil metabolism half-life ($t_{1/2}$) is 65 days (Department of Pesticide Regulation (DPR) 1994). The average $t_{1/2}$ of glyphosate in soil is 60 days or less, and after six months, typically about 90% of the compound is degraded to its natural components (Monsanto n.d.). The surfactants used in Roundup[®] have a $t_{1/2}$ of less than a week (Monsanto n.d.).

Glyphosate binds tightly to soil particles, with a K_{oc} of 6,922 cm³/g (DPR 1994). In a laboratory study, columns of soil treated with glyphosate were leached continuously with water for 45 days. Results demonstrated that none of the glyphosate was released from the soil (Monsanto n.d.). Only very small amounts of applied glyphosate are removed in runoff (USDA 1984).

The rate of degradation of glyphosate in water is generally slower than it is in most soils because there are fewer microorganisms in water. Hydrolysis $t_{1/2}$ is >35 days (DPR 1994). In turbid water, glyphosate adheres to particulate matter and is degraded by microorganisms (USDA 1984).

Solubility of glyphosate in water is 11,600 ppm at 25°C (Johnson 1991). The octanol/water partition coefficient for glyphosate is 0.0017 at 20 ppm and 0.0006 at 100 ppm, indicating virtually no tendency to bioconcentrate.

TOXICITY TO AQUATIC ORGANISMS

Toxicity to Aquatic Animals

One hundred nineteen toxicity tests on technical glyphosate and glyphosate formulations and twenty six toxicity tests on MON0818 were reviewed and found generally acceptable according to standards of the American Society of Testing and Materials (ASTM 1988). Toxicity tests on Rodeo^R also included X-77 surfactant. Other surfactants used with Rodeo^R may be more or less toxic than X-77. Test results are given in Appendices A and B.

Acute toxicity (LC_{50}) values (96-h unless noted) for technical glyphosate ranged from 10 mg/L for rainbow trout *Oncorhynchus mykiss* and chum salmon *O. keta* to 240 mg/L for rainbow trout (Appendix A-1). The LC_{50} values for Roundup^R ranged from 1.3 mg/L as glyphosate for rainbow trout to 55 mg/L as glyphosate for midge ^(48-h) *Chironomus plumosus* (Appendix A-2). Acute toxicity values for Rodeo^R ranged from 120 mg/L as glyphosate for coho salmon *O. kisutch* to 290 mg/L as glyphosate for chinook salmon *O. tshawytscha* (Appendix A-3). For toxicity tests on Rodeo^R, the test solution consisted of 31% Rodeo^R and 0.4% X-77 surfactant. The LC_{50} values for MON0818 ranged from 0.65 mg/L for rainbow trout to 13 mg/L for channel catfish *Ictalurus punctatus* and midge (Appendix A-4).

An investigation of the toxicity of Roundup^R to several species of frogs indicated LC_{50} values of >98 to >165 mg/L as glyphosate for adult frogs and LC_{50} values of 18.9 to 22.2 mg/L

as glyphosate for tadpoles (Bidwell and Gorrie 1995).

Table 1. Ranked acute toxicity ranges for technical grade glyphosate.

<u>Rank</u>	<u>Range (mg/L)</u>	<u>Species</u>
1	10 - 240	Rainbow trout <i>Oncorhynchus mykiss</i>
2	10 - 148	Chum salmon <i>Oncorhynchus keta</i>
3	14 - 190	Pink salmon <i>Oncorhynchus gorbuscha</i>
4	19 - 211	Chinook salmon <i>Oncorhynchus tshawytscha</i>
5	27 - 174	Coho salmon <i>Oncorhynchus kisutch</i>
6	55	Midge <i>Chironomus plumosus</i>
7	97	Fathead minnow <i>Pimephales promelas</i>
8	130	Channel catfish <i>Ictalurus punctatus</i>
9	135 - 220	Bluegill <i>Lepomis macrochirus</i>

Table 2. Ranked acute toxicity ranges for Roundup[®] (measured as glyphosate).

<u>Rank</u>	<u>Range (mg/L)</u>	<u>Species</u>
1	1.3 - 54.8	Rainbow trout <i>Oncorhynchus mykiss</i>
2	1.8 - 7.5	Bluegill <i>Lepomis macrochirus</i>
3	2.3 - 4.8	Fathead minnow <i>Pimephales promelas</i>
4	2.95	Cladoceran <i>Daphnia magna</i>
5	3.3 - 43	Channel catfish <i>Ictalurus punctatus</i>
6	7.0	Crayfish <i>Orconectes nais</i>
7	7.8	Cladoceran <i>Daphnia pulex</i>
8	8.1 - 8.7	Sockeye salmon <i>Oncorhynchus nerka</i>
9	9.6 - 33	Chinook salmon <i>Oncorhynchus tshawytscha</i>
10	10 - 33	Pink salmon <i>Oncorhynchus gorbuscha</i>
11	11 - 20	Chum salmon <i>Oncorhynchus keta</i>
12	11 - 32	Coho salmon <i>Oncorhynchus kisutch</i>
13	18 - 55	Midge <i>Chironomus plumosus</i>
14	43	Amphipod <i>Gammarus pseudolimnaeus</i>

Table 3. Ranked acute toxicity ranges for Rodeo^a (31%) and surfactant X-77 (0.4%) (measured as glyphosate)

<u>Rank</u>	<u>Range (mg/L)</u>	<u>Species</u>
1	120 - 200	Coho salmon <i>Oncorhynchus kisutch</i>
2	130 - 210	Rainbow trout <i>Oncorhynchus mykiss</i>
3	140 - 290	Chinook salmon <i>Oncorhynchus tshawytscha</i>

Table 4. Ranked acute toxicity ranges for MON0818.

<u>Rank</u>	<u>Range (mg/L)</u>	<u>Species</u>
1	0.65 - 7.4	Rainbow trout <i>Oncorhynchus mykiss</i>
2	1.0 - 3.0	Bluegill <i>Lepomis macrochirus</i>
3	1.0	Fathead minnow <i>Pimephales promelas</i>
4	1.4 - 2.7	Chum salmon <i>Oncorhynchus keta</i>
5	1.4 - 4.5	Pink salmon <i>Oncorhynchus gorbuscha</i>
6	1.7 - 2.8	Chinook salmon <i>Oncorhynchus tshawytscha</i>
7	1.8 - 4.6	Coho salmon <i>Oncorhynchus kisutch</i>
8	2.00	Cladoceran <i>Daphnia pulex</i>
9	2.60	Sockeye salmon <i>Oncorhynchus nerka</i>
10	13	Channel catfish <i>Ictalurus punctatus</i>

Aquatic organisms appear to be more sensitive to the surfactant used in Roundup[®], MON0818, than to glyphosate. The LC₅₀ values for technical glyphosate (Table 1) are between 10 and 100 times higher than those for surfactant MON0818 (Table 4) or for Roundup[®] (Table 2). Rodeo[®] does not contain the surfactant MON0818 that is included in the Roundup[®] formulation; Rodeo[®] with the surfactant X-77 (Table 3) has similar toxicity to technical grade glyphosate (Table 1).

Toxicity of glyphosate is highest in water with low pH and hardness, but toxicity of MON0818 is highest in water with higher pH and hardness.

Toxicity to Aquatic Plants

Glyphosate is a non-selective herbicide which has the potential to impact non-target plants. Roundup[®] EC₅₀ values for aquatic plants range from 2.0 mg/L for *Lemna minor* to 69.7 mg/L for periphytic algae (Appendix B). Toxicity values for aquatic plants were not available for technical grade glyphosate, Rodeo[®], or MON0818.

HAZARD ASSESSMENT

The formulation of glyphosate registered for use in aquatic sites is Rodeo[®]. Although Rodeo[®] is applied directly to target plants and not to water, it is possible that it will be introduced into aquatic environments during application, particularly during aerial applications. If Rodeo[®] is applied directly to water at the application rate of 7.5 pints/acre, the concentration of glyphosate in water will vary between 1.84 mg/L and 0.18 mg/L for depths of one and 10 feet, respectively. The lowest LC₅₀ value for Rodeo[®] (31%) with surfactant X-77 (0.4%) is 65 to 650 times greater than these values. When introduced into water, much of the glyphosate would adhere to particulate matter and would not be available for exposure to aquatic organisms. No invertebrate or amphibian toxicity tests were available for Rodeo[®]. However, invertebrates and amphibians appear to be less sensitive to technical glyphosate and Roundup[®] than are fish.

Given the low toxicity of Rodeo[®] to aquatic organisms, it should not pose a hazard to aquatic organisms when used according to the label. Roundup[®] was found to be moderately to slightly toxic to fish and invertebrates and its use near aquatic sites would be less desirable.

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Appendix A-1. Acute toxicity of technical glyphosate to aquatic organisms.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Bluegill <i>Lepomis macrochirus</i>	N/A	Glyphosate (96.7%)	96-h	LC ₅₀	7.4/44 6.5/44 9.5/44	135 140 220	Mayer and Ellersieck 1986
Channel catfish <i>Ictalurus punctatus</i>	N/A	Glyphosate (96.7%)	96-h	LC ₅₀	7.4/44	130	Mayer and Ellersieck 1986
Chinook salmon <i>Oncorhynchus tshawytscha</i>	juv	Glyphosate (88.5-96.4%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	19 30 211	Wan et al 1989
Chum salmon <i>Oncorhynchus keta</i>	juv	Glyphosate (88.5-96.4%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	10 22 148	Wan et al 1989
Coho salmon <i>Oncorhynchus kisutch</i>	juv	Glyphosate (88.5-96.4%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	27 36 174	Wan et al 1989
Fathead minnow <i>Pimephales promelas</i>	N/A	Glyphosate (96.7%)	96-h	LC ₅₀	7.4/44	97	Mayer and Ellersieck 1986
Midge <i>Chironomus plumosus</i>	larval	Glyphosate (technical)	48-h	EC ₅₀	7.2/40	55	Folmar et al 1979
Pink salmon <i>Oncorhynchus gorbuscha</i>	Juv	Glyphosate (88.5-96.4%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	14 23 190	Wan et al 1989
Rainbow trout <i>Oncorhynchus mykiss</i>	juv	Glyphosate (88.5-96.4%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	10 22 197	Wan et al 1989

Appendix A-1. Acute toxicity of technical glyphosate to aquatic organisms.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	Glyphosate (96.7%)	96-h	LC ₅₀	6.5/44 7.0/44 9.5/44	140 130 240	Mayer and Ellersieck 1986

Appendix A-2. Acute toxicity of Roundup[®] to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Amphipod <i>Gammarus pseudolimnaeus</i>	mature	Roundup [®]	96-h	LC50	7.4/272	43	Mayer and Ellersieck 1986
Bluegill <i>Lepomis macrochirus</i>	N/A	Roundup [®]	96-h	LC50	7.4/44 7.4/44 7.4/44 7.4/44 6.5/44 7.5/44 8.5/44 9.5/44 7.4/44 7.4/44 7.4/44 7.4/44 7.4/272	5.6 7.5 5.0 4.0 4.2 2.4 2.4 1.8 4.0 6.0 7.0 5.6 5.5	Mayer and Ellersieck 1986
Channel catfish <i>Ictalurus punctatus</i>	N/A	Roundup [®]	96-h	LC50	7.4/44 7.4/44	4.4 13	Mayer and Ellersieck 1986
Channel catfish <i>Ictalurus punctatus</i>	eyed egg	Roundup [®]	96-h	LC50	7.4/44	43	Mayer and Ellersieck 1986
Channel catfish <i>Ictalurus punctatus</i>	swimup fry	Roundup [®]	96-h	LC50	7.4/44	3.3	Mayer and Ellersieck 1986
Channel catfish <i>Ictalurus punctatus</i>	yolk-sac fry	Roundup [®]	96-h	LC50	7.4/44	4.3	Mayer and Ellersieck 1986
Chinook salmon <i>Oncorhynchus tshawytscha</i>	N/A	Roundup [®]	96-h	LC50	6.3/5.3 7.2/10 8.2/86	33 27 17	Wan et al 1989

Appendix A-2. Acute toxicity of Roundup[®] to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Chinook salmon <i>Oncorhynchus tshawytscha</i>	N/A	Roundup [®]	96-h	LC50	6.1/4.5	9.6	Mitchell et al 1987
Chum salmon <i>Oncorhynchus keta</i>	juv	Roundup [®]	96-h	LC50	6.3/5.3 7.2/10 8.2/86	20 19 11	Wan et al 1989
Cladoceran <i>Daphnia magna</i>	1st instar	Roundup [®]	48-h	EC50	7.4/272	2.95	Mayer and Ellersieck 1986
Cladoceran <i>Daphnia pulex</i>	<24-h	Roundup [®]	96-h	LC50	6.3/3-4	7.8	Servizi et al 1987
Coho salmon <i>Oncorhynchus kisutch</i>	juv	Roundup [®]	96-h	LC50	6.3/5.3 7.2/10 8.2/8.6	30 31 13	Wan et al 1991
Coho salmon <i>Oncorhynchus kisutch</i>	juv	Roundup [®]	96-h	LC50	6.3/5.3 7.2/10 8.2/8.6	32 27 13	Wan et al 1989
Coho salmon <i>Oncorhynchus kisutch</i>	juv	Roundup [®]	96-h	LC50	6.3/3-4	12.8	Servizi et al 1987
Coho salmon <i>Oncorhynchus kisutch</i>	N/A	Roundup [®]	96-h	LC50	6.2/4.5	11	Mitchell et al 1987
Crayfish <i>Orconectes nais</i>	mature	Roundup [®]	96-h	LC50	7.4/280	7.0	Mayer and Ellersieck 1986

Appendix A-2. Acute toxicity of Roundup[®] to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Fathead minnow <i>Pimephales promelas</i>	N/A	Roundup [®]	96-h	LC50	7.4/44 7.4/44 7.4/44 7.4/44	2.3 4.8 2.9 4.3	Mayer and Ellersieck 1986
Midge <i>Chironomus plumosus</i>	3rd instar	Roundup [®]	48-h	EC50	7.4/272	55	Mayer and Ellersieck 1986
Midge <i>Chironomus plumosus</i>	larval	Roundup [®]	48-h	EC50	7.2/40 7.2/40 7.2/40 7.2/40 7.2/40	18 43 34 34 30	Folmar et al 1979
Pink salmon <i>Oncorhynchus gorbuscha</i>	juv	Roundup [®]	96-h	LC50	6.3/4.8 7.5/38.9 8/80.5	31 10 14	Wan et al 1991
Pink salmon <i>Oncorhynchus gorbuscha</i>	juv	Roundup [®]	96-h	LC50	6.3/5.3 7.2/10 8.2/86	33 31 14	Wan et al 1989
Rainbow trout <i>Oncorhynchus mykiss</i>	juv	Roundup [®]	96-h	LC50	6.3/5.3 7.2/10 8.2/86	33 15 14	Wan et al 1989
Rainbow trout <i>Oncorhynchus mykiss</i>	juv	Roundup [®]	96-h	LC50	6.3/4.8 7.5/38.9 8/80.5	31 31 14	Wan et al 1991
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	Roundup [®]	96-h	LC50	7.2/40	8.3	Folmar et al 1979

Appendix A-2. Acute toxicity of Roundup[®] to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	Roundup [®]	96-h	LC50	6.1/4.5 7.6/85 7.7/81	12 11 7.4	Mitchell et al 1987
Rainbow trout <i>Oncorhynchus mykiss</i>	juv	Roundup [®]	96-h	LC50	6.3/3-4	8.5 7.8	Servizi et al 1987
Rainbow trout <i>Oncorhynchus mykiss</i>	juv	Roundup [®]	96-h	LC50	4.8-6.2/-- 6.7/--	54.8 52.0	Hildebrand et al 1982
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	Roundup [®]	96-h	LC50	7.4/44 7.4/44 7.4/44 7.4/44 7.4/44 7.4/44 6.5/44 7.5/44 8.5/44 9.5/44 7.4/44 7.4/44 7.4/44 7.4/44	7.6 1.3 8.3 14 7.5 7.4 7.6 1.6 1.4 1.4 9.0 7.6 7.6 7.6 3.4	Mayer and Ellersieck 1986
Rainbow trout <i>Oncorhynchus mykiss</i>	eyed egg sac fry swim up fingerling fingerling	Roundup [®]	96-h	LC50	7.2/40 7.2/40 7.2/40 7.2/40 7.2/40	16 3.4 2.4 1.3 8.3	Folmar et al 1979

Appendix A-2. Acute toxicity of Roundup[®] to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Sockeye salmon <i>Oncorhynchus nerka</i>	fingerling	Roundup [®]	96-h	LC50	7.95/84 8.00/84	8.1 8.4	Servizi et al 1987
Sockeye salmon <i>Oncorhynchus nerka</i>	fry	Roundup [®]	96-h	LC50	7.7/84	8.7	Servizi et al 1987

Appendix A-3. Acute toxicity of surfactant MON0818 to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Chinook salmon <i>Oncorhynchus tshawytscha</i>	juv	MON0818 (75%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	2.8 2.8 1.7	Wan et al 1989
Chum salmon <i>Oncorhynchus keta</i>	juv	MON0818 (75%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	2.7 2.4 1.4	Wan et al 1989
Coho salmon <i>Oncorhynchus kisutch</i>	juv	MON0818 (75%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	4.6 3.2 1.8	Wan et al 1989
Bluegill <i>Lepomis macrochirus</i>	N/A	MON0818	96-h	LC ₅₀	7.2/40 7.2/40 7.2/40	3.0 1.3 1.0	Folmar et al 1979
Channel catfish <i>Ictalurus punctatus</i>	N/A	MON0818	96-h	LC ₅₀	7.2/40	13	Folmar et al 1979
Cladoceran <i>Daphnia pulex</i>	<24-h	MON0818	96-h	EC ₅₀	7.8/84	2.00	Servizi et al 1987
Fathead minnow <i>Pimephales promelas</i>	N/A	MON0818	96-h	LC ₅₀	7.2/40	1.0	Folmar et al 1979
Midge <i>Chironomus plumosus</i>	larval	MON0818	48-h	EC ₅₀	7.2/40	13	Folmar et al 1979
Pink salmon <i>Oncorhynchus gorbuscha</i>	juv	MON0818 (75%)	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	4.5 2.8 1.4	Wan et al 1989

Appendix A-3. Acute toxicity of surfactant MON0818 to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Rainbow trout <i>Oncorhynchus mykiss</i>	juv	MON0818	96-h	LC ₅₀	6.3/5.3 7.2/10 8.2/86	2.0 2.5 1.7	Wan et al 1989
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	MON0818	96-h	LC ₅₀	6.5/-- 9.5/-- 7.2/40	7.4 0.65 2.0	Folmar et al 1979
Sockeye salmon <i>Oncorhynchus nerka</i>	fry	MON0818	96-h	LC ₅₀	7.9/84	2.60	Servizi et al 1987

Appendix A-4. Acute toxicity of Rodeo[®] (31%) and surfactant X-77 (0.4%) to aquatic animals.

Species	Life Stage	Formulation	Test Length	Effect	ph/hardness	Values (mg/L)	Reference
Chinook salmon <i>Oncorhynchus tshawytscha</i>	N/A	Rodeo [®] (with X-77 surfactant)	96-h	LC ₅₀	5.8/5.0 7.4/77	140 290	Mitchell et al 1987
Coho salmon <i>Oncorhynchus kisutch</i>	N/A	Rodeo [®] (with X-77 surfactant)	96-h	LC ₅₀	5.8/5.0 6.2/4.5	200 120	Mitchell et al 1987
Rainbow trout <i>Oncorhynchus mykiss</i>	N/A	Rodeo [®] (with X-77 surfactant)	96-h	LC ₅₀	6.0/5.0 7.8/75	130 210	Mitchell et al 1987

Appendix B. Toxicity of glyphosate to aquatic plants.

Species	Formulation	Test Length	Effect	Value (mg/L)	Reference
Aquatic bacteria	Roundup [®]	30-d	growth inhibition	50	Chan and Leung 1986
Duckweed <i>Lemna minor</i>	Roundup [®]	14-d	growth inhibition	2	Hartman and Martin 1984
Periphytic algae	Roundup [®]	44-52-d	photosynthesis inhibition	35.4 45 69.7	Goldsborough and Brown 1988